Health Mobilization Series J-1

Manual for Protection of Public Water Supplies from Chemical Agents

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE • Public Health Service

Acknowledgment

We wish to acknowledge the assistance and cooperation given us in the preparation of this manual by the U.S. Army, Edgewood Arsenal, Chemical Research and Development Laboratories.

Health Mobilization Series J–1

Manual for Protection of Public Water Supplies from Chemical Agents

U.S. DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
Public Health Service
Division of Health Mobilization
1965

Public Health Service Publication No. 1071–J–1

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C., 20402 - Price 15 cents

CONTENTS

INTRODUCTION

This manual offers basic information for water works and public health personnel concerning the potential hazard to public water supplies from chemical agents and the practical detection and treatment measures to cope with hazards from chemical agents.

Every water-works operator should know these essentials to protect public water supplies from the effects of chemical agents. However, since the detection and treatment of toxic chemical agents in water involves complex chemical problems, it is essential that evaluation should be made by an experienced chemist. Public water supply systems should arrange to have the services of a skilled chemist available for civil defense purposes, if one is not already on the staff. Competent chemists are often available in local industries, colleges, and private laboratories.

Detection methods, tests, and treatment measures described herein are considered the best now available. Simplified test procedures are under development but have not reached the stage where they can be released. As new or improved techniques are developed, they will be included in revisions of this manual.

Specific references for recommended reading for more detailed and specific technical information on the various agents of military significance are listed in *Bibliography* (p. 21). Additional information can also be obtained from local and State civil defense and health agencies, and from the regional offices of the U.S. Public Health Service.

None of the information in this manual is classified, therefore it may be reproduced and distributed as needed.

CHEMICAL AGENTS

A. DEFINITION

A chemical agent is a chemical compound intended for use as a tactical or strategic weapon. It may be directed against humans, plants, or animals. The chemical agents described in this manual are those known agents which might be used against the human population.

B. POTENTIAL USES AND TYPES OF CHEMICAL AGENTS

Chemical attacks may precede a nuclear attack to impair retaliatory and defensive capability, accompany an initial nuclear attack, or follow in subsequent attacks to further demoralize the surviving population. Adequate preparation in terms of preventive and protective measures, education, and training, and provision of detection and treatment measures can greatly minimize the effects of such attacks.

Chemical agents in vapor or aerosols are most likely, and detection and symptoms, personnel protective measures and decontamination procedures for equipment and clothing should be known to all water works operators and superintendents.

The four groups of chemical agents considered of interest are tabulated in two categories on page 3.

CHEMICAL AGENTS

More Likely Hazards

Group	Symbol	Name	Action	Water treatment
1. Nerve Agents	.....	Organo-phosphorus compounds	Cholinesterase inhibitor.	Treat with heavy chlorine dosages—dechlorinate with activated carbon.
2. Mustards	HD	Sulfur mustard	Vesicant	Carbon, coagulation, settling and chlorination.
	HN–I	Nitrogen mustard	do	
	HN–2	do	do	
	HN–3	do	do	

Less Likely Hazards

Group	Symbol	Name	Action	Water treatment
3. Arsenicals	L	Lewisite	Vesicant	Carbon, coagulation, settling and chlorination.
	ED	Ethyldichloroarsine	do	
4. Cyanides	AC	(1) Hydrogen cyanide	Systemic	(1) Aeration and chlorination if adequate ventilation available.
	CK	(2) Cyanogen chloride	do	(2) Coagulation and filtration. (*See* Cyanides, p. 20).

PUBLIC WATER SUPPLIES

A. VULNERABILITY OF SUPPLY SYSTEMS

1. Raw Water Reservoirs

Deliberate contamination of raw water reservoirs is not a likelihood. Relatively large quantities of agents would be required; storage and standard water treatment will significantly reduce the toxic fraction of most of the chemical agents known at this time; and the opportunity for detection would be greatest if introduced ahead of the treatment plant.

Accidental contamination of a reservoir could occur from a weapon falling into or in very close proximity to it; and possibly, but least likely, from rainfall through an aerosol or vapor, or runoff from heavily contaminated land areas. Accidental spills resulting from highway or waterway transportation of chemicals may also contaminate water sources.

2. Treatment Plants

Physical security and detection measures are likely to be at their best at treatment plants. Therefore they are less likely to be subject to undetected contamination from either deliberate or accidental means.

3. Distribution System

The points at which agents could be deliberately and most effectively introduced would be within the distribution system, where physical protection and detection is most difficult, and smaller quantities of toxic agents would be required for effect. It is likely that sabotage through a water supply would be directed at installations of major importance for command and direction rather than at the general population.

B. PHYSICAL PROTECTION OF SUPPLY

If a period of tension should develop and time permits such actions, the following measures should be given careful consideration:

1. Patrols

Patrolling or guarding the water purification plant, reservoirs, pumping stations, water storage tanks, etc. Frequent checks should be made wherever construction or maintenance work is being done. If unusual activities are noticed, ascertain that the project is authorized and the personnel involved are cleared.

2. Barriers

Fencing may be erected around the most sensitive areas such as the water purification plant, pumping stations, well sources, reservoirs, water storage tanks, chemical storehouses, etc.

3. Personnel Surveillance

Alertness and care should be exercised in permitting visitors to the water works plant, pumping stations, and similar installations. All authorized personnel should be advised to report any unusual visitors or actions.

C. DETECTION OF CHEMICAL AGENTS

1. Investigations of Death and Illness

Unless a warning has been received, or a detection system has been established, the first indication of attack may be a sudden onset of deaths and illnesses with toxic symptomatology. Epidemiological investigations should be conducted to determine the contaminated area and possibly the point of contamination. The medical and laboratory investigators should try to determine the type of contaminant to establish treatment or other protective measures.

2. Sampling

Samples should be taken from locations which are suspect because of epidemiological investigations or at such other points as may be determined feasible for introduction of contaminants.

Samples should be kept at approximately the same temperature and pH conditions as when taken, until laboratory tests are made. When a chemical attack is suspected, or imminent, samples should be taken at least every hour, and preferably every half-hour depending upon how fast the operator can perform the necessary chemical tests.

3. Laboratory Methods

Plans should be made for the sampling and testing, using standard chemical analytical procedure and equipment, that will give the most rapid

results. Reagents should be prepared and kept in readiness insofar as practicable, and the procedures practiced to maintain laboratory techniques. Electronic equipment should be tested frequently and kept in working order. The recommended tests and their interpretations outlined in *Detection Measures* (p. 9) should be studied carefully.

4. Health Department Liaison

Maintenance of close liaison with local health departments is important. Consultation with these agencies will help determine whether a local outbreak of death or illness may be the result of biological or chemical agents, and also indicate the source of contamination.

D. ACTION IF CONTAMINATION IS SUSPECTED

If contamination of the water supply by chemical agents is suspected, a course of action similar to the following protective program should be taken:

1. Public Warning

The public should be advised *immediately* not to use water from the public water supply system until further notice.

2. Water Shutoffs

Shut off water where it enters distribution system or cut off any part of the system suspected of contamination until laboratory tests can be completed. This is a drastic action, and before the step is taken, the question of water for fire protection and other essential uses must be given careful consideration. Conditions will vary for practically every water system and decisions will have to be made "on the spot" in accordance with the situation at the time the action is contemplated.

3. Sampling

Samples should be taken throughout the system for analysis. The sampling patterns and schedules should be developed in advance. Practice is essential.

4. Physical Security

To the extent practicable, vulnerable points of the system should be protected by physical security measures.

E. TREATMENT AND DISTRIBUTION

Until the system is determined to be clear of contamination and proper protective and/or corrective measures have been put into effect, the public should use water stored in containers for civil defense purposes. If this is not available, water should be distributed by tank trucks or other emergency methods from another water source known to be safe or from some point or points on the system known to be safe. The following steps should be taken:

1. *Raw Water Free of Chemical Agents*

If the raw water is known to be free of chemical agents, the normal treatment given the supply is acceptable.

2. *Raw Water Suspected of Contamination*

If contamination of raw water is suspected, the selection of proper treatment is dependent upon the type of agent or agents used. If the agents can be identified by specific laboratory tests, the appropriate treatment measures can be applied, as given under *Treatment Measures and Tolerance Limits* (p. 18). It is more likely, however, that the exact agent is not known (i.e., an approximate test may show that nerve agents are present but may not identify the specific agent). The type of treatment shown in *Treatment Measures and Tolerance Limits* (p. 18) generally can be determined immediately by results of the chlorine demand test. Select treatment as follows:

(a) If the Chlorine Demand Test, *Detection Measures* (p. 9), is positive, adjust pH of a sample of the raw water to 7.0 and chlorinate with free chlorine or calcium hypochlorite* to 40 ppm available chlorine. Allow 30 minutes contact time. Dechlorinate with activated carbon. Test for chemical agents in accordance with the appropriate tests out-

*A combination of chlorine dioxide and free chlorine or calcium hypochlorite is more effective in treatment of some nerve agents than is chlorine or hypochlorite alone. If chlorine dioxide is available, it should be used in combination with free chlorine. Also, the use of compounds containing nitrogen (for example, ammonium salts) should be avoided, inasmuch as they react with free chlorine to form chloramines which are ineffective against nerve agents.

lined in *Detection Measures* (p. 9). If tests indicate insufficient reduction of the toxic material, re-run jar test using more chlorine (up to 100 ppm) and if necessary, give longer contact time.

(b) If there is not an unusual chlorine demand, add lime or soda ash to a 500-ml sample until pH is raised above 9.5. Allow to stand 30 minutes. To a 100-ml aliquot, add alum to reduce pH and to coagulate. Allow to settle and then test for presence of chemical agents.

If the concentration of agent has been reduced, but not to an acceptable level for human consumption, repeat the procedure on a second 100-ml portion of the sample. Note the total time the sample has remained at pH 9.5. *Repeat until the level of contaminant is acceptable* in accordance with procedure.

Tolerance Limits for Drinking Water

Nerve agents	5 ppb (parts per billion)
Mustard agents	5 ppm (parts per million)
Arsenicals	5 ppm (parts per million)
Lewisite	as arsenic
Ethyldichloroarsine	
Cyanides	25 ppm (parts per million)

(c) If contamination is detected or suspected in any part of the water system, particularly in transmission and distribution piping, service lines, etc., the entire system should be checked carefully. Those parts of the system showing contamination should, if possible, be segregated from the remainder of the system to prevent further diffusion of contamination. Contaminated water should be wasted or disposed of by drainage or pumping to eliminate any danger from the contaminants.

Cooperation of the water users may be necessary for flushing of service and distribution lines. The populace should be warned periodically that water should not be used for any purpose until notified of its safety. Water that is contaminated should be disposed of in such a manner that it will not create new hazards. Operating personnel, who may come in contact with the contaminated water, should be warned of the hazards and informed of methods for personal treatment if dangerously exposed.

DETECTION MEASURES

A. RAPID CHLORINE DEMAND TEST

1. Method

For this detection, use tests outlined in *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes.**

2. Interpretation of Results

Positive chlorine demand tests in raw water may be due to many natural agents in water, such as hydrogen sulfide and organic or bacterial contamination. In addition, it may also indicate the presence of sulfur mustard and its hydrolytic product, arsenicals, some nerve agents, and free cyanide from hydrogen cyanide. Other nerve agents or their hydrolytic products do not exert a chlorine demand. Nitrogen mustard and its hydrolytic agents do not exert a chlorine demand at low pH. In treated water (finished) having no chlorine demand immediately prior to contamination, sulfur mustard or Lewisite exerts a chlorine demand that is equivalent to the amount of agent added.

3. pH Determination

Most chemical agents hydrolyze to some degree in water giving an acid hydrolysis product. The degree of hydrolysis is dependent upon the agent, temperature, pH, and time. *Water having pH 6 or lower should be strongly suspected of contamination and should not be used until confirmed otherwise.*

B. DETERMINATION OF NERVE AGENTS IN WATER

Note: ***Tolerance limit 5 parts per billion.***

1. Theory of the Test

In this test, the water solution containing the nerve agent is allowed to react with the enzyme cholinesterase for 5 minutes at 25° C and pH 7.2.

*Prepared and published jointly by American Public Health Association, American Water Works Association, and the Federation of Sewage & Industrial Wastes Association, 11th Edition, 1960.

After this time, part of the enzyme becomes inactivated. The rest is available for catalyzing the hydrolysis of a substrate acetylcholine chloride. This may be written schematically as in the following reactions.

a. Reactions

(1) Enzyme cholinesterase + Nerve agent $\xrightarrow[\text{pH } 7.2]{\text{5 min. @ 25° C}}$ Inhibited enzyme + Unreacted enzyme

(2) Unreacted enzyme + Substrate (acetylcholine chloride) $\xrightarrow[\text{pH } 7.2]{\text{10 min. @ 25° C}}$ Choline + Acetic acid + Enzyme

The hydrolysis of the acetylcholine chloride proceeds at a rate which is proportional to the concentration of unreacted enzyme. Then hydroxylamine is added to convert the unreacted acetylcholine chloride to acethydroxamic acid, which is measured as a ferric complex. From the amount of complex (rust colored), the concentration of anticholinesterase material present in original solution can be estimated. This may be written schematically as in the following reactions.

(3) Excess substrate + Hydroxylamine $\xrightarrow{\text{pH ca } 12}$ Acethydroxamic acid

(4) Acethydroxamic acid + Ferric ion $\xrightarrow{\text{pH } (1.0\text{–}1.4)}$ Ferric complex of acethydroxamic acid (rust colored compound)

2. Stock Solutions

Note: *Stock solutions are indicated by upper case letters (e.g., SOLN. A, SOLN. B, etc.).*

a. Phosphate buffer (0.134M, pH 7.2)—(SOLN. A)

Mix 7 parts of a solution containing 23.8 g $Na_2HPO_4 \cdot 2H_2O$ diluted with distilled water to equal 1 liter and 3 parts of a solution containing 18.2 g KH_2PO_4 diluted with distilled water to equal 1 liter. The pH is adjusted to 7.2—if necessary—by the addition of a few drops of 1*N* HCl or 1*N* NaOH.

b. Acetylcholine chloride (0.04M)*—(SOLN. B)

Dissolve 300 mg of acetylcholine chloride in 41 ml of distilled water.

Acetylcholine chloride may be obtained in 100-mg quantities in sealed glass ampules (Merck & Co., Inc.). Use three ampules, rinsing with measured volume of the distilled water.

c. Hydroxylamine hydrochloride (2M)*—(SOLN. C)

Dissolve 27.8 g of hydroxylamine hydrochloride and dilute with distilled water to equal 200 ml.

*Keep under refrigeration when not in use.

d. *Potassium chloride* (0.6*M*)—(SOLN. D)
Dissolve 44.8 g KCl and dilute with distilled water to equal 1 liter.

e. *Enzyme stabilizer solution—(SOLN. E)**
Dissolve 0.1 g gelatin in 20 ml warm distilled water. Cool, add 6 ml SOLN. A, 50 ml SOLN. D, and dilute with distilled water to equal 100 ml. Adjust to pH 7.4 with NaOH.

f. *Enzyme solution—(SOLN. F)**
Weigh accurately about 0.1 g acetylcholinesterase (purified stabilized acetylcholinesterase from bovine erythrocytes, 20,000 units, Winthrop Laboratories). Add a sufficient volume of SOLN. E (adjusted to pH 7.4 prior to use) so that the enzyme concentration is equal to 0.100 g/20 ml.

g. *Sodium hydroxide* (3.5*M*)—(SOLN. G)
Dissolve 140 g NaOH in distilled water, cool, and dilute to equal 1 liter.

3. Working Solutions

***Note:** Working solutions are indicated by lower case letters (e.g., soln. a, soln. b, etc.). These working solutions should be prepared on day of use.*

a. *Enzyme—(soln. a)**

Dilute 1 ml SOLN. F with SOLN. A to equal 50 ml. Warm to 25° C before use by letting approximately 15 ml set in the constant temperature bath for 10 to 15 minutes.

b. *Acetylcholine chloride—(soln. b)**

Add 5 ml SOLN. B to 25 ml SOLN. D and dilute with distilled water to equal 50 ml. Warm to 25° C before use by letting approximately 15 ml set in the constant temperature bath for 10 to 15 minutes.

c. *Basic hydroxylamine—(soln. c)**

Mix 50 ml SOLN. C with 50 ml SOLN. G. *Use cold.*

d. *Ferric chloride in hydrochloric acid*—(soln. d)

Dissolve 133 g $FeCl_3 \cdot 6H_2O$ in approximately 500 ml distilled water, add 235 ml concentratd hydrochloric acid and dilute with distilled water to equal 2 liters. This solution may be prepared in advance and stored cold until needed.

*Keep under refrigeration when not in use.

4. Apparatus

The following items are required:

Constant temperature water bath at 25° C.

Klett-Summerson photoelectric colorimeter with 540 mμ filter.*

Dry 10-ml Klett tubes, previously calibrated with water at 540 mμ.

Glass rods for mixing solutions.

Stopwatch.

Fast draining 1-, 2-, and 3-ml volumetric pipets.

Miscellaneous glassware as required.

5. Procedure

a. Adjustment of blank (tube A) and control (tube B) readings

Before applying this test to samples of unknowns, it may be necessary to adjust concentrations of *working solutions* a and b. Run the following tests:

(1) To each of 2 Klett tubes, add 3 ml distilled water. Label tubes A and B.

(2) To tube A only, add 1 ml soln. a. Let drain 15 seconds. Mix while adding.

(3) After *exactly* 5 minutes, add 1 ml of soln. b to tube A. Allow 15 seconds for draining. Mix with stirring rod while adding. After 30 seconds add 1 ml soln. b to tube B.

(4) After *exactly* 10 minutes more (15 minutes on the stopwatch), add 2 ml soln. c to each tube at the same 30-second intervals. Mix as before.

(5) One minute after the hydroxylamine has been added, add 1 ml soln. a to tube B.

(6) After 5 minutes more (20 minutes on stopwatch), add 3 ml soln. d to each tube, mixing thoroughly while adding the reagent.

(7) Read in colorimeter at 540 mμ after 3 to 6 minutes. Be sure there are no bubbles in the reading area of the tube.

*If this equipment is not available, use a spectrophotometer or photoelectric colorimeter equipped to measure absorbency at 540 mμ.

The reading given by tube B *must* fall between 240 and 260 units. If the reading is less than 240, add small increments of SOLN. B to soln. b and re-run. If the reading is more than 260, dilute soln. b with 0.3*M* KCl (made by diluting SOLN. D 1: 1 with water).

The reading given by tube A *must* be between 90 and 100 units. If the reading is more than 100, add small increments of SOLN. F to soln. a.

On standing, the activity of SOLN. F may decrease. Higher volumes of SOLN. F will be required to obtain the correct blank readings. When the volume required reaches 2 ml, prepare a fresh stock of SOLN. F.

b. *Preparation of unknown samples for testing*

(1) If the solution contains carbon, filter to obtain a clear solution.

(2) If the solution contains chlorine, determine the amount of 0.05–0.1*N* sodium thiosulfate required to give no residual chlorine by orthotolidine test using an aliquot of unknown. Add this volume of thiosulfate to a fresh equal aliquot of the unknown.

(3) Adjust the pH of the sample to 6–8 by the addition of small amounts of dilute HCl or NaOH if necessary.

(4) Pipet 2 ml of the adjusted sample into 10 ml of distilled water, mix well and proceed as directed under (3) below.

c. *Testing of unknown samples*

(1) Place maximum of 11 Klett tubes in the test tube rack.

(2) To 9 (or fewer) tubes, add 3-ml samples of unknowns prepared as directed in b. above. To the last two tubes (No. 10=blank, and No. 11=control), add 3 ml distilled water. Place a stirring rod in each tube and place the rack in the constant temperature bath. Wait several minutes to allow samples to reach 25° C.

(3) Add 1 ml soln. a to the first 10 tubes in order, at 30-second intervals, starting the stopwatch as the enzyme is added to the first tube. Allow 15 seconds for drainage and mix gently while adding the enzyme solution.

(4) Follow the procedure described in *Procedure* (steps (3) through (7), p. 12),* adding each reagent to the first sample at the time indicated and to each successive sample at 30-second intervals thereafter.

*Tube No. 11 (control) is treated as tube B in *Procedure* (step (5), p. 12).

d. Interpretation of results

Samples of unknows which give readings of 60 or more Klett-units higher than the blank readings contain dangerous quantities of nerve agent.

C. DETERMINATION OF MUSTARDS IN WATER

Note: *Tolerance limit 5 parts per million.*

1. Reagents

(a) Hydrochloric acid; dilute 1: 50.

(b) DB–3 reagent; 5% gamma-(4-nitrobenzyl) pyridine in acetone.

(c) Acetone; ACS specifications.

(d) Potassium carbonate; 0.1*M* solution.

(e) Standard nitrogen mustard (HN3) solution. This solution must be fresh and must be prepared immediately before use.

2. Procedure—Photometric Method

Prepare a series of HN3 standards containing up to 60 micrograms per 4 ml of distilled water (pH 4). Develop color in same manner as sample. Determine optical densities of the standards and sample in a Klett-Summerson photometer using 10-ml Klett tubes and a No. 66 (660 millimicrons) filter. One microgram of HN3 is equivalent to approximately 2.0 Klett-units.

Take a sample of the unknown and develop color as follows and compare to standards.

(a) Adjust pH of 100 ml of the sample to 4.0±0.2 by addition of a few drops of dilute HCl; also adjust 100 ml of distilled or deionized water to the same pH.

(b) Pipet exactly 4.0 ml of suspected water (or an aliquot diluted to 4.0 ml with distilled water adjusted to pH 4) into a test tube. Sample should contain less than 0.060 mg HN3 or 0.080 mg HD per 4 ml.

(c) Prepare a reagent blank (4 ml distilled water adjusted to pH 4) and treat in same manner as sample.

(d) To sample and blank, add exactly 0.5 ml of DB–3 reagent and mix until cloudiness is evenly distributed. Appearance of a yellow color at this step indicates presence of cyanogen chloride.

(e) Place the tubes in a boiling water bath for 10 minutes. If the sample is high in hardness, heat for 15 minutes in bath.

(f) Cool under tap water.

(g) Add 4 ml of acetone and 0.5 of 0.1*M* potassium carbonate. Mix thoroughly.

(h) Determine the density of the color exactly 5 minutes after the addition of the last reagent. The relationship of color density to concentration of agent can be determined by comparison with the prepared standards.

D. DETERMINATION OF ARSENICALS IN WATER

Note: ***Tolerance limit 5 parts per million—as arsenic.***

1. Reagents

(a) Sodium perborate*; 1% aqueous solution, prepare fresh daily.

(b) Potassium bisulfate solution; 8.2% aqueous.

(c) Hydrazine sulfate; 0.6% aqueous solution.

(d) Ammonium molybdate; 1% in 4.5*N* sulfuric acid.

2. Procedure—Molybdenum Blue Method

(a) With Klett-Summerson photometer, prepare a series of standards containing 20, 30, 40, and 50 ppm Lewisite or their equivalent in arsenic concentration. Mg Lewisite X 0.3613 is equivalent to mg arsenic, or mg arsenic X 2.823 is equivalent to mg Lewisite. Develop color in same manner as sample. Read absorbance in photometer using 10-ml Klett tubes and No. 66 filter (660-mμ wavelength).

(b) Pipet 2-ml aliquot of sample into a test tube and dilute to 4.0 ml with distilled water.

(c) Prepare a blank of 4.0 ml of distilled water and treat in same manner as sample.

(d) To each add 2 drops of potassium bisulfate and 0.5 ml of sodium perborate.

(e) Mix and place in boiling water bath for 20 minutes.

(f) Add 0.5 ml of hydrazine sulfate and 0.5 ml of ammonium molybdate reagent.

*With low-ratio alkalinity, such as du Pont's *Perdox*.

(g) Mix and continue heating in water bath for 5 minutes more.

(h) Cool, dilute to 10 ml with distilled water, read in the photometer and compare with the prepared standards.

3. Interpretation of Results

Water samples high in phosphates or silicates may give false positive results. If they are suspected, repeat the test, omitting the addition of sodium perborate reagent. When this reagent is omitted, the organic arsenic will not be converted to the proper form to give color reaction. Any color formed in this control test is attributed to phosphates or silicates. The difference between the two readings represents the true concentration of arsenicals in the sample.

E. DETERMINATION OF CYANIDE OR CYANOGEN CHLORIDE (CK) IN WATER

Note: ***Tolerance limit 25 parts per million.***

1. Reagents

(a) Standard chloramine T; 5% aqueous solution.

(b) Sodium arsenite; 0.455% aqueous solution.

(c) Acetone; ACS specifications.

(d) DB–3 reagent; 5% gamma-(4-nitrobenzyl) pyridine in acetone.

(e) Standard cyanide solution; 0.251 g KCN per liter water, 0.1 mg cyanide per ml; or Hellige color comparator disc No. 860–12.

2. Procedure

(a) Determine chlorine demand on 100-ml aliquot of sample. If the demand is more than 10 ppm, reduce the demand of 100 ml of the sample by addition of a calculated amount of standard chloramine T solution (cf. *Rapid Chlorine Demand Test,* page 9).

(b) Pipet 5.0 ml of the sample (chlorine demand less than 10 ppm) into a 13-mm cell or Klett tube.

(c) Add 0.1 ml of 5% chloramine T solution followed immediately by addition of 1 ml of sodium arsenite.

(d) After ½ minute, add 0.5 ml of DB–3 reagent and 1.5 ml of acetone.

(e) Dilute to 10 ml with distilled water and mix.

(f) After 5 minutes (and not later than 10 minutes) compare color density with Hellige standard chlorine disc (No. 860–12) or in a Klett-Summerson photometer with a series of cyanide standards.

3. Standards for Comparison

a. *Hellige comparator with standard chlorine disc.*

Place sample in center compartment and blank (sample without reagents) in right-hand compartment. Match color of sample with one on the disc and record results in ppm chlorine.

Reading on chlorine disk:	*Equivalent ppm cyanide*
0.1	0.5
0.15	1.0
0.25	2.0
0.50	5.0
1.0	15.0
1.5	40.0
2.5	60.0
5.0	80.0
10.0	100.0

b. *Klett-Summerson photometer.*

Prepare a series of cyanide standards containing from 0.0 to 0.0005 mg of CN^- in 5-ml volumes. Develop color of the standards in the same manner as the sample, starting with the addition of 0.1 ml 5% chloramine T. Determine the optical densities of the standards and the sample in the photometer, using 10-ml Klett tubes and a No. 42 filter (420-mμ wavelength).

4. Interpretation of Results

A positive cyanide test indicates the possible contamination with CN^-, CK, and/or one of the nerve agents. If CK is suspected from formation of yellow color in the mustard test, the following determination for CK should be made: Repeat the above procedure for cyanides on sample without satisfying the chlorine demand and omit the addition of chloramine T and of sodium arsenite. The final results are in ppm cyanide due to CK. To convert to ppm CK, multiply the results in ppm cyanide by the factor 2.4.

TREATMENT MEASURES AND TOLERANCE LIMITS

A. NERVE AGENTS

Anticholinesterase agents can be treated effectively by heavy chlorination followed by application of activated carbon, which acts as a dechlorinating agent as well as absorbing products from hydrolyzing the nerve agents.

1. Tolerance Limits

Nerve agents should be reduced to at least 5 parts per billion (ppb) in drinking water to be safe for human consumption. In the anticholinesterase test, outlined in *Detection Measures* (p. 9), this requires a reading of less than 60 Klett-units greater than the blank reading.

2. Treatment Procedure

(a) Add free chlorine or calcium hypochlorite until a residual of at least 40 ppm is obtained.

***Note:** A combination of chlorine dioxide and free chlorine or calcium hypochlorite is more effective in treatment of some nerve agents than is chlorine or hypochlorite alone. If chlorine dioxide is available, it should be used in combination with free chlorine. Also, the use of compounds containing nitrogen (for example, ammonium salts) should be avoided, inasmuch as they react with free chlorine to form chloramines which are ineffective against nerve agents.*

(b) If the pH of the sample following chlorination is less than 7, adjust to a pH of approximately 7.

(c) Allow 30 minutes contact time.

(d) Add enough activated carbon to dechlorinate.

(e) Test for presence of nerve agents with standard test.

(f) If test indicates insufficient reduction, add free chlorine or calcium hypochlorite to 100 ppm, allow up to 2 hours' contact time, and repeat test procedure.

B. MUSTARD AND LEWISITE

Mustard agent is soluble in water to the extent of 800 ppm at 20° C. Mustard agent in water will be distributed into a surface film, a water-soluble fraction, and an undissolved portion. The undissolved fraction may settle and remain unchanged for several weeks at the bottom. The soluble fraction will be hydrolyzed, the rate of hydrolysis depending upon the quantity of agent, the temperature, and the alkalinity of the water. Boiling destroys mustard in 15 to 30 minutes, but 2 or 3 days are required if storage at ordinary temperature is used.

Water containing 500 ppm or more of mustard is impractical to treat for drinking purposes.

1. Treatment Procedures

For the removal of mustard and Lewisite from water, the following treatment is recommended.

(a) Treat the contaminated water with activated carbon (300 mesh) in the following doses:

(1) For Lewisite, 30 ppm carbon for each ppm Lewisite.

(2) For mustard, 30 ppm carbon for each ppm mustard.

(3) For nitrogen mustard, 60 ppm carbon for each ppm nitrogen mustard.

(b) Mix the carbon and water for 20 minutes to insure complete absorption of the agent by the carbon.

(c) Add 175 ppm of coagulant to the carbon-dosed water and enough soda ash to give optimal coagulation.

(d) After thorough, gentle mixing, allow the water to coagulate and clarify by sedimentation for 30 minutes.

(e) Filter the water at a slow enough rate to ensure good filtration.

(f) Chlorinate beyond the breakpoint.

(g) The final concentrations should be:

(1) *Not more than 5 ppm.*

(2) *pH should be above 5.*

(3) Chlorine demand, less than 5 ppm.

(4) There should be no chemical odor or taste.

C. ETHYLDICHLOROARSINE (ED)

This arsenical is rapidly hydrolyzed in water into soluble products which are also toxic. Treatment methods used for mustard and Lewisite will work for this contaminant. Final concentrations should be 5 ppm or less.

D. CYANIDES

Note: ***The human tolerance limits for cyanogen chloride (CK) or hydrogen cyanide (AC) are 25 ppm.***

Cyanogen chloride hydrolyzes slowly in water forming cyanates which readily decompose into harmless products. A concentration of 50 ppm will be hydrolyzed to 25 ppm in about a week.

Hydrocyanic acid and many of the cyanide salts are very soluble in water and do not react appreciably with it. Cyanides are not removed by carbon treatment. Cyanide can be removed by treatment of water in the neutral to alkaline pH range with ferrous or ferric salts, to precipitate the cyanides as Prussian blue which can be removed by coagulation and filtration. As long as an excess of iron salts is used, any blue color coming through the filter would be nontoxic. Both cyanide and cyanogen chloride are destroyed by heavy dosages of chlorine.

BIBLIOGRAPHY

Effects of Chemical Warfare Agents for Use in Readiness Planning. Emergency Manual Guide, No. HEW–3, OS, USDHEW. 1959. 17 pp. Washington, D.C., 20201.

Chemical, Biological, and Radiological Warfare Agents and Fallout Effects on Water Supplies (Lecture) Health Mobilization Course Manual, USDHEW. March 1961, Washington, D.C., 20201.

Chemical Warfare (Lecture) Health Mobilization Course Manual, USDHEW. April 1964. Washington, D.C., 20201.

Methods for the Detection and Identification of CW Agents in Aqueous Carriers, USDHEW, PHS No. 529. Kamphake, Lawrence J.; Kabler, Paul W.; Robert A. Taft Sanitary Engineering Center, January 1957. Cincinnati, Ohio.

Nerve Gas in Public Water, Epstein, J., M.S. Public Health Reports, Vol. 71, No. 10, October 1956. USDHEW, PHS, Washington, D.C., 20201.

Signs and Symptoms of Nerve Gas Poisoning (Lecture) Health Mobilization Course Manual, USDHEW. May 1960. Washington, D.C., 20201.

U.S. GOVERNMENT PRINTING OFFICE: 1965 O—766-545

Publications in the Health Mobilization Series are keyed by the following subject categories:

A—Emergency Health Service Planning

B—Environmental Health

C—Medical Care and Treatment

D—Training

E—Health Resources Evaluation

F—Packaged Disaster Hospitals*

G—Health Facilities

H—Supplies and Equipment

I—Health Manpower

J—Public Water Supply

*Formerly called Civil Defense Emergency Hospitals.

Public Health Service
Publication No. 1071 J-1